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I, LEANNE MYNOTT, MANAGER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. PQ 1094 for a patent by ADELAIDE BRIGHTON MANAGEMENT LIMITED filed on 21 June 1999.

WITNESS my hand this
Thirty-first day of January 2002

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PROVISIONAL SPECIFICATION

APPLICANT: **ADELAIDE BRIGHTON MANAGEMENT LIMITED**

Invention Title: **SAMPLE PRESENTATION FOR X-RAY DIFFRACTION**

The invention is described in the following statement:

SAMPLE PRESENTATION FOR X-RAY DIFFRACTION

This invention relates to a method and apparatus for continuously presenting a sample from a stream of crystalline particulate material for obtaining X-ray diffraction (XRD) analyses of the material. The invention is particularly applicable for phase composition analysis of cement and cement clinker and will be described in relation to this application, however it is to be understood the invention is applicable for analysing other crystalline materials, such as for example from mineral processing streams.

In the manufacture of cement, feedstock materials such as limestone, shale, sand and iron oxide are blended and then fired in a kiln from which cement clinker is derived. The cement clinker with some additives, is then milled to produce cement. The milling, which is the final stage in manufacturing cement, is carried out in a ball mill, ie a rotary mill which contains a charge of steel balls. As the mill rotates the input materials (mainly cement clinker) and small amounts of additives such as gypsum, limestone and sometimes fly ash) are ground and mixed to a fine state or powder.

X-ray diffraction measurements may be made on the cement clinker from the kiln, the clinker being suitably cooled and crushed to a fine powder for the measurements. Such measurements can provide information on the ratios between the different clinker phases and on the percentage of free lime. The strength of a final cement product is significantly determined by these phase ratios, and the amount of free lime is an indicator of the degree of clinkering. Thus such X-ray diffraction measurements, if available on line, would provide information which can be used to control the kiln operation.

X-ray diffraction measurements may also be made on the cement powder from the mill. These can provide information on the ratios of gypsum and other additives in the cement, information about crystal phases in the cement clinker, and on the degree of dehydration of the gypsum. Such ratios also affect the

strength of the final cement product and the degree of dehydration affects the cement setting time. Thus, if these measurements were available on-line, information would be provided which can be used to control the milling and thus the quality of the final cement product.

Heretofore, X-ray diffraction measurements of ex-kiln cement clinker and ex-mill cement powder have been laboratory based. For such measurements, a sample of the process stream, which may be taken automatically or by hand, is delivered to the laboratory where individual sample pellets, of the order of only a few grams, are prepared and presented to the XRD machine, either by hand or using robotics. The time taken for such sample preparation and measurement limits the usefulness of the information for process control. Furthermore, the extra grinding required to reduce the particle size to enable static samples to be analysed by the X-ray analysis may cause changes in the dehydration states for milled cement.

An object of the present invention is to provide for presentation of a sample from a process stream for X-ray diffraction measurements to be taken on a timely and continuous basis such that the measurements are available for action to be taken to control the process. It is also an object of the invention to provide a method for X-ray diffraction analysis on a continuous material stream.

According to a first aspect, the invention provides a method for continuously presenting a sample from a stream of crystalline particulate material for obtaining X-ray diffraction analyses of the particulate material, including,

continuously extracting a sample from the stream of particulate material,

feeding the sample onto a continuously moving carrier and smoothing and flattening its surface,

continuously moving the carrier through a station for performing X-ray diffraction measurements on said smooth and flat sample surface, and

continuously removing the sample from the carrier prior to feeding further sample onto the carrier.

Preferably the sample is formed into a bed on the moving carrier and more preferably the carrier includes an endless groove for receiving the sample and into which the sample is preferably packed to form the bed.

Using this invention, extra grinding of the ex-mill cement sample is not required because the moving sample presented to an X-ray diffraction machine ensures that even with larger particle sizes, a suitable number of particles can be expected to be oriented in such ways as to fulfil the Bragg condition for reflection from every possible interplanar spacing. Preferably the sample is fed onto the carrier at a rate such that the groove is overfilled, in which case excess sample is removed from the carrier and the sample in the groove suitably presented for packing thereinto.

According to a second aspect, the invention provides apparatus for presenting a sample from a stream of crystalline particulate material for X-ray diffraction measurements including,

a carrier for receiving a continuous feed of the material, the carrier being drivable for continuous movement,

means for preparing the sample on the carrier and for smoothing and flattening its surface,

and wherein the carrier is such that the said sample is removed, or the apparatus includes means for removing said sample therefrom, as the carrier moves, the removal of the sample occurring prior to where the carrier receives the feed of sample and after the sample passes a measurement station.

Preferably the carrier includes an endless groove and the means for preparing the sample packs the sample into the groove. Preferably the apparatus includes means for removing excess sample from the carrier before the sample is packed into the groove.

Preferably the apparatus further includes an X-ray generator and detector for taking X-ray diffraction spectra of the packed sample in the groove. Preferably the detector is position sensitive detector.

The method may be performed on (and the apparatus positioned for) cement clinker which exits the kiln, in which case some of the clinker needs to be cooled and crushed to a powder to provide the stream of particulate material from which a sample is continuously extracted and fed onto the carrier.

The method may also or alternatively be performed on (and the apparatus positioned for) cement powder which exits the finish mill. Using this invention, extra grinding of the ex-mill cement sample is not required because the moving sample presented to an X-ray diffraction machine ensures that even with larger particle sizes, a suitable number of particles can be expected to be oriented in such ways as to fulfil the Bragg condition for reflection from every possible interplanar spacing.

The continuous withdrawal of a sample from the process stream allows its analysis on a continuous basis and thus the provision of current product data on which decisions can be made to control the process. Such control may be effected automatically, for example as in a closed loop feedback system, or manually by a process operator.

According to a third aspect the invention provides a method for X-ray diffraction measurements for analysis of a stream of crystalline particulate material, including

continuously extracting a sample from the stream of particulate material,

preparing the continuous sample stream for X-ray diffraction measurements and conveying the so prepared stream through a measurement station,

directing an X-ray beam onto the continuous material stream as it passes through the measurement station and detecting reflected X-rays using a position sensitive (area) detector to provide diffraction spectra for the continuous sample.

Preferably the X-ray diffraction spectra are analysed according to the Rietveld method.

The term "continuous" and similar terms such as "continuously" or "continually" as used herein, are to be understood as meaning that the steps or measurements as so qualified apply for the duration of a discrete measurement cycle, which cycle may not be continuous in itself. That is, the invention encompasses the use of a number of sequential and discrete measurement cycles, with the above described steps of the method applying for each discrete cycle, as well as a measurement cycle which is long term and thus may be said to be "continuous" in itself.

The carrier is preferably a horizontally orientated wheel or table which is mounted for rotation about a vertical axis, with the above-mentioned endless groove being an annular groove formed in an upper surface thereof. However, other configurations for the carrier are possible, for example an endless belt type conveyor which may have a longitudinal groove formed in its outer facing surface. For a carrier in the form of a rotatable carrier, the apparatus will include means for removing the packed sample from the carrier groove, which means may be an appropriately shaped stationary scraper for scooping the groove clean as the carrier rotates, or a suitable suction device. For a carrier in the form of an endless conveyor, the sample may fall off as the conveyor turns through 180° to follow its return path and may additionally include an appropriate scraper or other device to assist removal of the sample.

The packing of the sample into the endless groove accompanied by a smoothing and flattening of its surface is preferably accomplished by a driven roller which is positioned over the endless groove. The apparatus preferably

further includes a rotatable brush for cleaning the roller. However the invention encompasses other forms of devices for such packing, for example a spatula.

XRD analysis of minerals is only able to analyse the crystals of the material largely at the surface of the sample presented to the XRD instrumentation and as the focus of the X-ray beam on the sample is tight, for example an area of the order of 4 mm^2, the more sample that is presented for analysis, the higher the confidence that the result is representative of the material in the process stream. The present invention, in providing a continuous sample supply, is a significant improvement over the prior art where only a single pellet of a few grams is periodically prepared and analysed. It is also important for accuracy that the sample surface be very smooth and flat, for example for a sample of powder which gives a residue on a 40 micron screen of less than 20% and can be delivered for analysis at less than 100°C, the surface should be smooth and flat to within 10 microns. The preferred form of device for packing and flattening the sample within the endless groove, namely a driven roller, provides for such accuracy.

For a better understanding of the invention and to show how it may be carried into effect, an embodiment thereof will now be described, by way of non-limiting example only, with reference to the accompanying drawings.

In the drawings

Fig. 1 is a diagrammatic representation of the main components of an example apparatus according to the invention.

Fig. 2 is a plan view of apparatus according to an embodiment of the invention.

Fig. 3 is an elevation view of the apparatus of Fig. 2.

Fig. 4 is a section on line B-B of Fig. 2.

Fig. 5 shows typical output results for XRD analysis of cement.

The same reference numeral is used on the various figures to illustrate the same component.

With reference to Fig. 1, the schematically illustrated apparatus includes a carrier in the form of a horizontally orientated wheel 10 which is mounted for rotation in an anti-clockwise direction 12 about a vertical axis 14 by a driving means 16. The wheel 10 includes a flat upper surface 18 in which an annular groove 20 is formed. A feeding means 22 is located for continuously feeding a particulate sample 24 onto surface 18 to overfill groove 20 as wheel 10 rotates. A scraper blade 23 is located to remove excess sample from the surface 18 prior to the sample being packed into the groove 20.

Means for packing the sample 24 into the groove 20 and smoothing and flattening its surface is a driven roller 26 which is located above the groove 20. Roller 26 is also driven for rotation in an anti-clockwise direction 28 by driving means 16. The outer facing curved surface 30 of roller 26 is precision ground and the roller is driven such that the speed of surface 30 is the same as that of surface 18 at the groove 20. Thus the roller presses on the sample surface as presented from scraper 23 to pack the sample 24 into the groove 20 and provide it with a smooth and flat surface 31 to the desired accuracy without any speed differential between that surface 31 and the contacting surface 30. A roller brush 32 is also provided to clean the precision surface 30 of roller 26 to remove any sample that may adhere to it.

The wheel 10 then moves through a measurement station which includes an X-ray generator 34 and position sensitive detector 36. A suitable processor means 38 presents the measurements in a desired format. Use of a position sensitive detector is preferred, although use of other types of detector, such as a single point detector combined with a goniometer to measure angular displacement, is possible. The X-ray diffraction instrumentation is described in more detail below.

Following its passage through the measurement station, the sample 24 in groove 20 is removed by a scraper arrangement 40 prior to further sample 24 being fed onto the carrier wheel 10. The sample material which is removed from carrier wheel 10 by scrapers 23 and 40 is collected and extracted from the apparatus for example by a vacuum device as represented by reference 42.

Carrier 10 also includes a precision height adjustment device 44 as accurate positioning of the surface 31 of the bed of sample 24 is required for the X-ray diffraction analysis as represented by line 45 for an incident X-ray beam and line 46 for the reflected rays.

Example XRD instrumentation consists of the following -

(i) INEL 3kw X-ray generator (34) with RS232 interface to power the XRD tube.

(ii) Philips, cobalt target, long fine focus XRD tube rated at 1800W.

(iii) Graphite monochromator to remove unwanted wavelengths and 0.2x8mm slits to define the beam size at the sample.

(iv) INEL CPS120 position sensitive detector (36) to detect the XRD pattern plus a panel of electronics to process signals from the detector.

(v) Industrial computer (38) built into the system to control data collection, analysis and result reporting.

Data is collected using software specifically designed and coded for interaction with the INEL detector 36. Data can be collected for times ranging from 1 to 1000 seconds and summed over as many data sets as deemed necessary to obtain appropriate counting statistics. One example of such settings are 60 second data collections with 10 data sets summed for analysis providing analyses every minute after the first 10 minutes.

The XRD data is analysed using the “whole pattern” or Rietveld based approach. Fig. 5 is a table of typical output results.

The apparatus of the invention is preferably located (and consequently the method performed) in an airconditioned room to avoid instrument distortion due to temperature changes and to ensure protection of the electronic equipment. A representative sample of a product stream can be conveyed into such a room located in proximity to the product stream.

The embodiment of apparatus according to the invention as shown by Figs. 2 to 4 does not include the XRD instrumentation.

The invention described herein is susceptible to variations, modifications and/or additions other than those specifically described and it is to be understood that the invention includes all such variations, modifications and/or additions which fall within the spirit and scope of the above description.

DATED: 21 June, 1999

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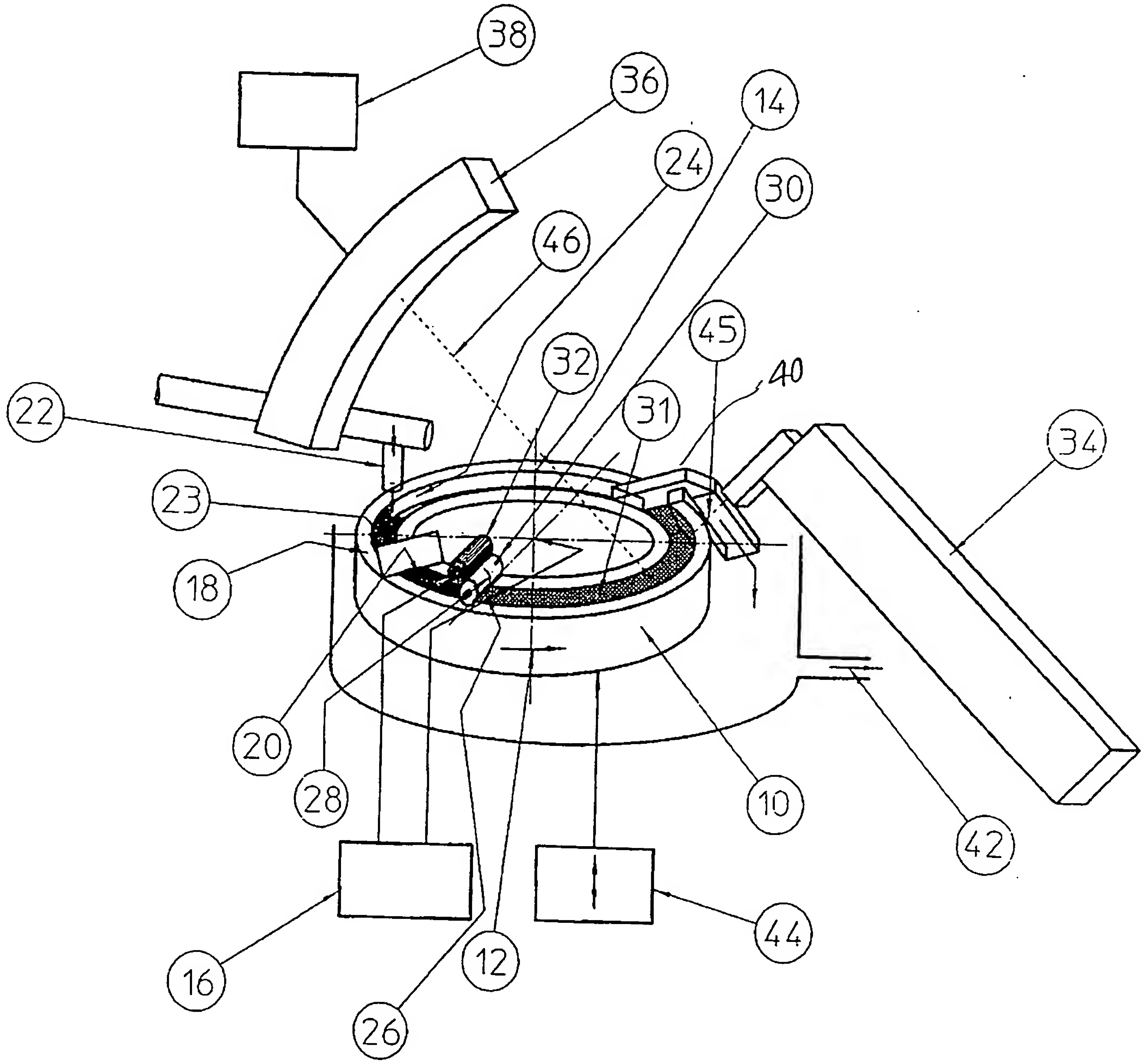

FIG 1

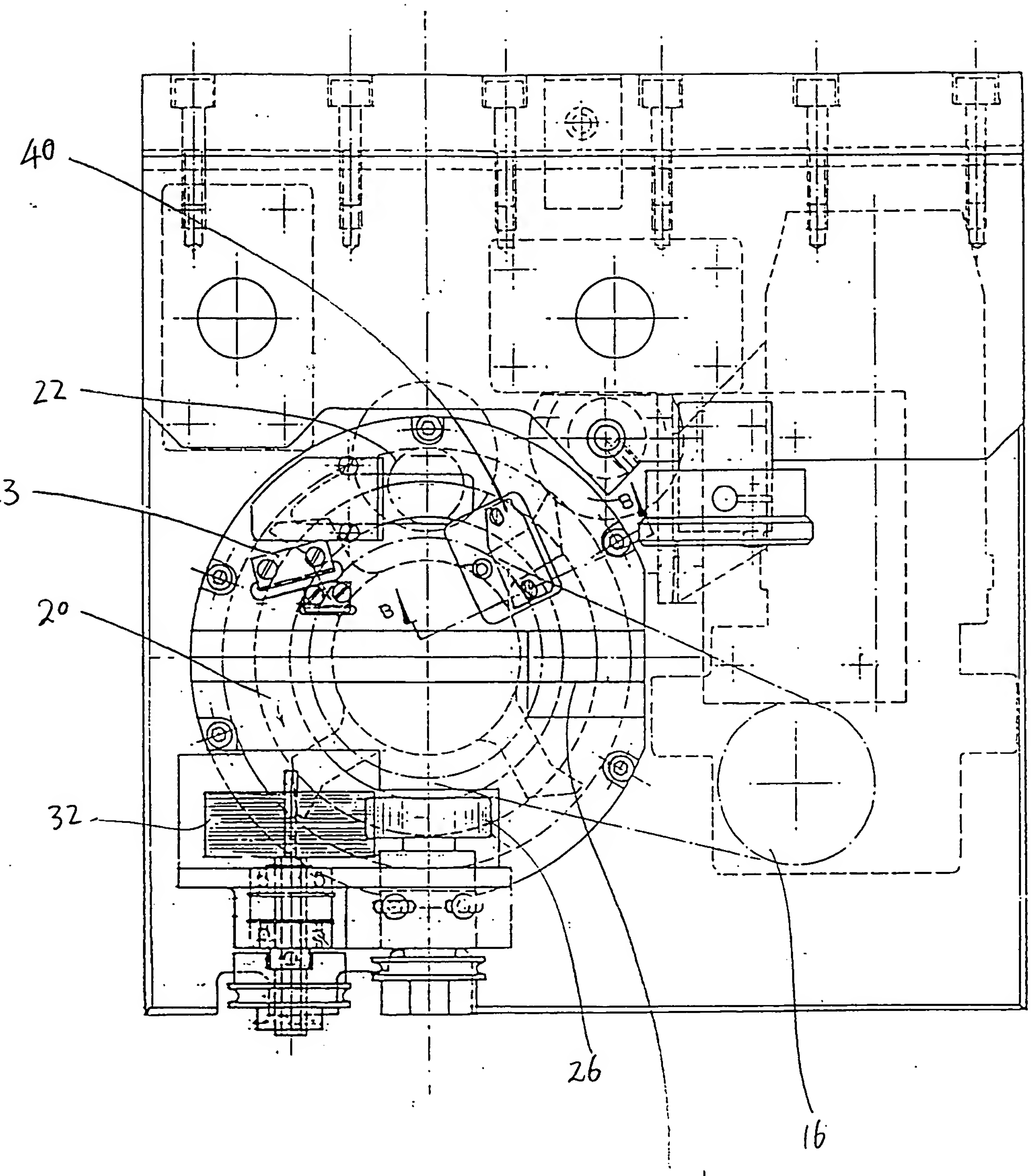

FIG 2

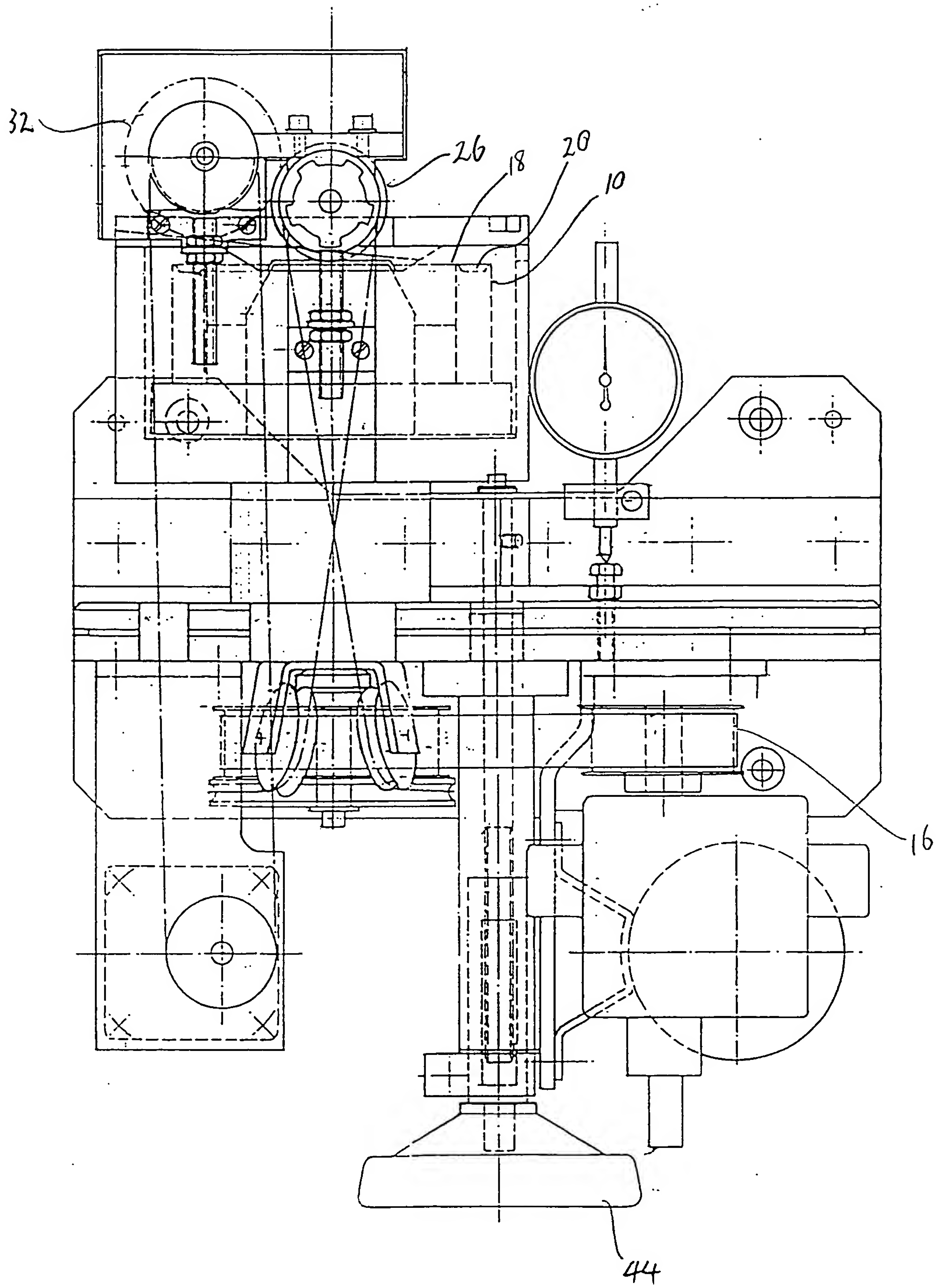

FIG 3

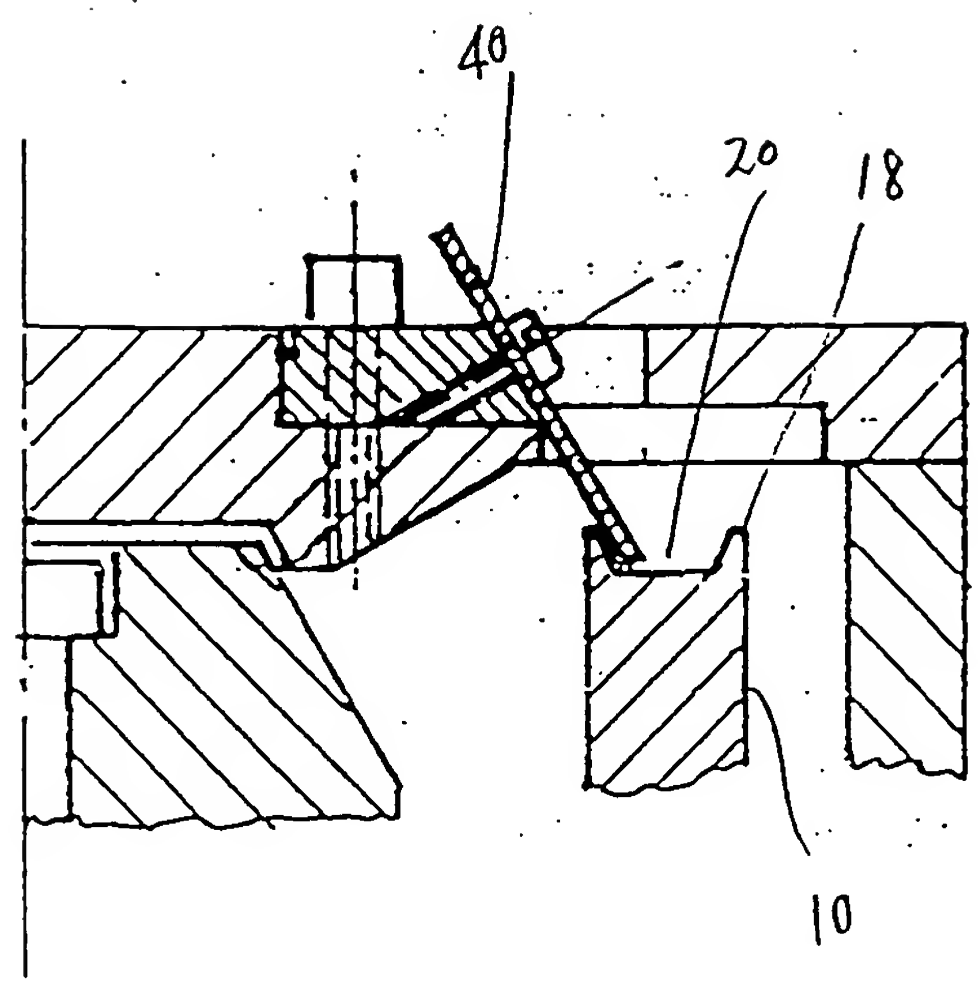

FIG 4

Sample BH-T2-67 sample date 9-11/5/99 115 C

Date Time	Batch No	Alite	Belite	Ferrite-a	Ferrite-b	Aluminate	Aluminate	Lime	Portlandit	Gypsum	Hemihydr	Anhydrite
5/12/99 11:50	12599	66.796	6.637	4.931	8.11	6.666	0.116	0.207	0.451	3.287	2.48	0.001
5/12/99 11:51	12599	65.113	7.308	5.082	8.213	6.668	0.129	0.069	1.562	3.052	2.273	0.001
5/12/99 11:53	12599	65.72	6.142	6.604	6.254	6.545	0.147	0.222	0.691	3.323	2.414	0
5/12/99 11:54	12599	66.521	6.299	6.684	6.089	6.714	0.005	0.068	0.667	3.224	2.228	0
5/12/99 11:56	12599	66.594	5.894	5.87	7.475	7.152	0.347	0	1.061	3.05	2.595	0.01
5/12/99 11:57	12599	66.986	5.583	5.186	8.161	7.474	0.175	0.123	0.841	3.101	2.190	0
5/12/99 11:59	12599	67.506	6.427	5.036	7.797	6.32	0.203	0.074	1.241	2.845	1.998	0
5/12/99 12:00	12599	67.136	6.328	5.079	7.88	6.898	0.315	0.284	1.008	2.981	1.613	0
5/12/99 12:02	12599	65.474	7.87	6.188	6.047	6.389	0.005	0.124	1.425	3.107	2.203	0.01
5/12/99 12:03	12599	67.384	6.436	5.801	7.051	7.418	0.007	0.098	0.702	2.977	1.799	0.002

Calcite	Quartz	R Factor	CaO	SiO2	Al2O3	Fe2O3	MgO	TiO2	SO3	Na2O	K2O	Loss
0.001	0.418	11.592	65.384	20.063	5.102	3.745	1.009	0.14	2.897	0.173	0.221	0.952
0.093	0.345	11.81	65.454	19.803	5.178	3.801	1.007	0.142	2.674	0.178	0.231	1.2
1.429	0.448	11.657	65.212	19.626	5.064	3.705	0.990	0.138	2.877	0.172	0.216	1.042
1.075	0.424	11.733	65.382	19.874	5.052	3.683	0.997	0.137	2.728	0.173	0.217	1.448
0.015	0.135	11.72	65.504	19.83	5.336	3.798	1.015	0.141	2.856	0.187	0.227	1.064
0.093	0.079	11.557	65.828	19.848	5.417	3.849	1.025	0.143	2.655	0.19	0.227	1.031
0.007	0.454	11.547	65.77	20.177	5.021	3.697	1.006	0.137	2.425	0.169	0.216	1.024
0.045	0.433	11.574	65.776	20.08	5.231	3.753	1.014	0.139	2.276	0.182	0.226	0.989
0.787	0.372	11.877	65.602	20.071	4.865	3.561	0.975	0.131	2.666	0.169	0.224	1.479
0.053	0.272	12.243	65.752	20.187	5.271	3.744	1.014	0.138	2.378	0.186	0.229	0.929

FIG 5

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